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Expanding Family of π-Conjugated Trinuclear Dithiolenes: The Cases of Group 8 (Ru^{II}) and 10 (Ni^{II} and Pt^{II}) Metals

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S *Supporting Information*

ABSTRACT: New π-conjugated trinuclear dithiolenes with group 8 (**6**, Ru^{II}) and 10 (**7** and **8**, Ni^{II} and Pt^{II}) metals were synthesized. Compounds **6** and **7** exhibited intense electronic communication through the phenylene bridge among the three dithiolene moieties during oxidation of the metalladithiolene rings, which has not been confirmed in the analogous family of group 9 metals, **1**−**5**. Compound **8** exhibited an intense absorption band across the visible and near-IR regions, which was assigned as a charge transfer to the diimine and was red-shifted and broadened compared to the corresponding band of the mononuclear complex.

The research target of identifying synthetic routes to multinuclear metal complexes and organometallics that meet the needs for enhanced precise tuning of functionalities in the corresponding mononuclear complexes remains a challenge: For example, ferromagnetism, energy-transfer cascades, and electronic communication in mixed-valent states have been pursued.[1] Multinuclear transition-metal complexes and organometallics with intense electronic communication have attracted much attention from chemists: For example, triangular copper motifs play a crucial role in enzymes, such as ascorbate oxidase and laccase.[2] On the other hand, the square-shaped tetraferrocenyl molecule can act as a molecular quantum cellular automaton.[3]

Metalladithiolenes are some of the best compounds for pursuing metal integration because of their intriguing electrochemical and photochemical properties.[4] Both metal- and ligand-centered redox properties may be achieved in these compounds. Metalladithiolenes displaying ligand-centered redox properties yield high conductivities and unique magnetic properties.[4] One of the most striking examples of the photochemical reactivity was identified in diiminedithiolatoplatinum(II) complexes.[5] This class of complexes shows a charge-transfer-to-diimine band at long wavelengths in the visible region, which makes the compounds excellent sensitizers in dye-sensitized solar cells[6] or hydrogen evolution systems.[7] The red shift of this charge-transfer band toward the near-IR (NIR) region would benefit these applications because the proportion of solar radiation in this region is not trivial.

Under the background described above, we have investigated multinuclearization of metalladithiolenes.[8−10] One such class of compounds involves π-conjugated trinuclear dithiolenes with group 9 metals (**1**−**5**; Figure 1).[9,10] Initially, Co^{III} trinuclear complexes **1** and **2** were synthesized by trimerization of the corresponding monomer and were found to display peculiar magnetic properties (a matrix-induced spin-state change in $\mathbf{1}^{3-}$).[9] We then modified the synthetic procedure by introducing substitution of the halogen on the metal ions with (hexathiolato)benzene. This method opened the door to **3**−**5**, which include a more bulky (pentamethyl)cyclopentadienyl ligand bound to either Rh^{III} or Ir^{III}, as well as Co^{III}.[10] All three compounds displayed intense electronic communication in monoanionic and dianionic species. The reduction of dithiolenes comprising group 9 metals is practically metal-centered.[10] In contrast, electronic communication in the monocationic and dicationic states, in which the positive charges mainly lie on the dithiolato ligands and which would enhance the intriguing properties of dithiolenes described above, was not found in **3**−**5** because of the instability of the cationic species.[11]

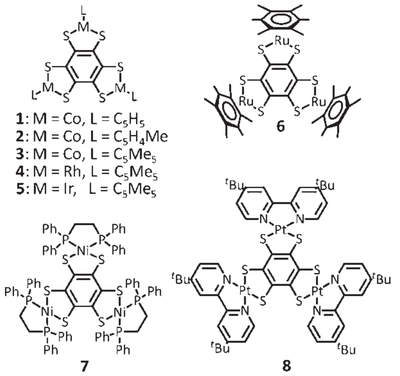

Figure 1. Phenylene-bridged π-conjugated trinuclear dithiolenes.

In this Communication, we extend the family of phenylene-bridged π-conjugated trinuclear dithiolenes to include group 8 (Ru^{II}, **6**) and 10 (Ni^{II} and Pt^{II}, **7** and **8**) metal complexes (Figure 1). Compound **6**, in particular, which includes a divalent group 8 metal, has an electronic structure identical with those of **1**−**5** with trivalent group 9 metals. Compounds **6** and **7** showed intense electronic communication in the mixed-valent cationic states, whereas **8** showed a red-shifted and broadened band corresponding to charge-transfer-to-diimine, covering the visible and NIR regions.

Compounds **6**−**8** were obtained from hexamercaptobenzene and the corresponding metal sources upon treatment with a base (see the Supporting Information for details). The low yields (**6**, 5%; **7**, 14%; **8**, 1%) came from decomposition in the course of alumina column chromatography rather than incomplete or random complexation. These complexes were characterized using ^1H NMR spectroscopy and high-resolution electrospray ionization time-of-flight mass spectrometry. Compounds **6** and **7**

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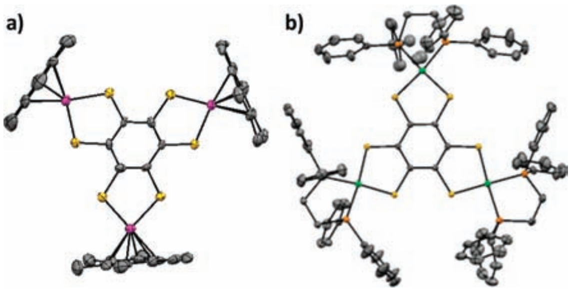

Figure 2. ORTEP drawings (gray, C; yellow, S; pink, Ru; orange, P; green, Ni; hydrogen atoms and crystal solvent molecules are omitted for clarity): (a) $6\cdot C_6H_{12}$; (b) $7\cdot 8CH_3CN$.

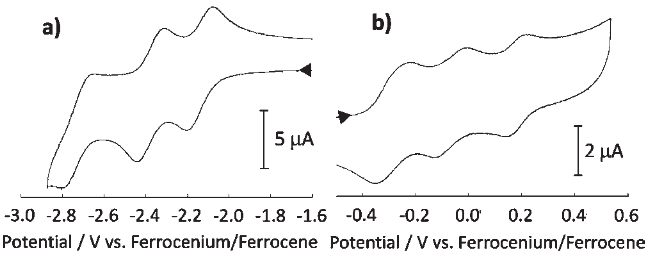

Figure 3. Cyclic voltammogram of **6** (0.5 mM) at a sweep rate of 0.1 V s^{-1}: (a) in 0.1 M n-Bu_4NClO_4—THF; (b) 0.1 M n-Bu_4NClO_4—PhCN.

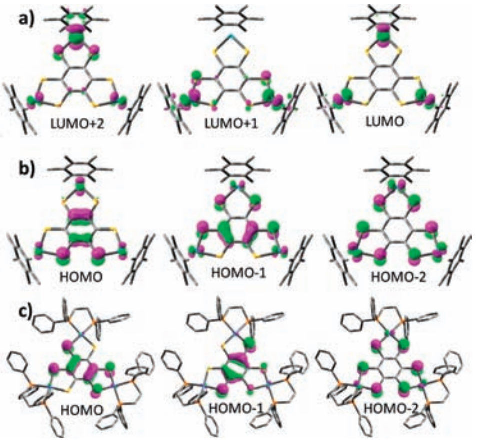

Figure 4. Frontier orbitals from DFT calculations: (a) LUMOs of **6**; (b) HOMOs of **6**; (c) HOMOs of **7**.

Table 1. Formal Potentials and Comproportionation Constants for the Reductions of 3—6

	potential/V vs ferrocenium/ferrocene			comproportionation constant	
	$E^{\circ\prime}$ (X^{2-}/X^{3-})	$E^{\circ\prime}$ (X^{-}/X^{2-})	$E^{\circ\prime}$ (X/X^{-})	log $K_c(X^{2-})$	log $K_c(X^{-})$
6	−2.73	−2.38	−2.14	5.9	4.0
3[a]	−1.92	−1.58	−1.35	5.8	3.9
4[a]	−2.18	−1.93	−1.74	4.2	3.2
5[a]	−2.35	−2.21	−2.12	2.4	1.5

[a] Ref 11.

were characterized by single-crystal X-ray structure analysis to determine the trinuclear configuration in a planar coordination environment (Figure 2).

Figure 3 shows the cyclic voltammograms of **6**. Three successive reversible redox waves were observed (Figure 3a), similar to those of **3**—**5**. This was consistent with the fact that the electronic structures of **6** and **3**—**5** were identical. The stepwise reductions of **3**—**5** were assigned to the reductions of the three metal centers, accompanied by intense electronic communication.[10] A density functional theory (DFT) calculation was performed for **6**. LUMO, LUMO+1, and LUMO+2 (Figure 4a) were mainly localized on the Ru ion centers, which assured the metal-centered character of the three reductions. A comproportionation constant, K_c, which is a parameter that describes the electronic communication in mixed-valent compounds, is defined as follows:[12]

$$K_c(\mathbf{X}^n) = [\mathbf{X}^n]^2/[\mathbf{X}^{n-1}][\mathbf{X}^{n+1}]$$
$$= \exp\{[E^{\circ\prime}(\mathbf{X}^{n+1}/\mathbf{X}^n) - E^{\circ\prime}(\mathbf{X}^n/\mathbf{X}^{n-1})]F/RT\} \quad (1)$$

where [**X**] is the concentration of a chemical species **X**, n is the valent state of **X**, which underwent comproportionation, and $E^{\circ\prime}(\mathbf{X}^n/\mathbf{X}^{n-1})$ is the formal potential of the $\mathbf{X}^n/\mathbf{X}^{n-1}$ redox couple. $E^{\circ\prime}$ and log K_c of **6** and **3**—**5**, for $n = -2$ and -1, are tabulated in Table 1. The data series indicated that the metal centers of **6** strongly communicated with one another.

The critical difference between **6** and **3**—**5** is that **6** can be reversibly oxidized on the time scale of cyclic voltammetry (Figure 3b). According to the DFT calculation, the oxidation reactions originated from the ruthenadithiolene π orbitals (Figure 4b). A large K_c was observed, indicative of intense electronic communication among the three dithiolene rings (Table 2). Compound **7** also gave two reversible redox waves upon oxidation within the observed potential window (Figure 5 and Table 2). A DFT calculation for **7** assigned these oxidations as nickelladithiolene-centered (Figure 4c). This result was consistent with previous reports for mononuclear complexes.[13] A large K_c indicated the presence of intense electronic communication, at least in the monocationic form, 7^+. On the other hand, **8** gave an irreversible voltammogram with multiple oxidations (data not shown).

Figure 6 shows the electronic spectra of **7**, **8**, and the mononuclear Pt(bdt)(dbbpy) (bdt = 1,2-benzenedithiolate; dbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) in dichloromethane. Compound **7** did not absorb significantly in the visible region, whereas the other compounds displayed characteristic absorptions assignable to charge-transfer-to-diimine.[5] The charge-transfer-to-diimine band in **8** [λ_{max} = 624 nm, ε_{max} = 16 100 M^{-1} cm^{-1}, and fwhm = 5710 cm^{-1} (fwhm = full width half-maximum)] was red-shifted and broadened compared to that of Pt(bdt)(dbbpy) (λ_{max} = 555 nm, ε_{max} = 8740 M^{-1} cm^{-1}, and fwhm = 3840 cm^{-1}), possibly stemming from the intense π conjugation among the three dithiolene rings through the phenylene bridge. This is consistent with the intense electronic communication in **7**, which has an electronic structure identical with that of **8**. We note that **6** showed an intense visible band that was assignable to a ligand-to-metal charge-transfer band (Figure S1 in the Supporting Information).[14]

In conclusion, we expanded the family of phenylene-bridged π-conjugated trinuclear dithiolenes to include group 8 (**6**, Ru^{II}) and 10 (**7** and **8**, Ni^{II} and Pt^{II}) metals. Compounds **6** and **7** showed intense electronic communication in the cationic states, in which positive charges were distributed over the metalladithiolene

Table 2. Formal Potentials and Comproportionation Constant Values for the Oxidation of 6 and 7

	potential/V vs ferrocenium/ferrocene			comproportionation constant	
	$E^{\circ\prime}$ (X^+/X^0)	$E^{\circ\prime}$ (X^{2+}/X^+)	$E^{\circ\prime}$ (X^{3+}/X^{2+})	log $K_c(X^+)$	log $K_c(X^{2+})$
6	−0.29	−0.07	0.18	3.7	4.2
7	−0.50	0.03	[a]	9.0	

[a] Out of the potential window.

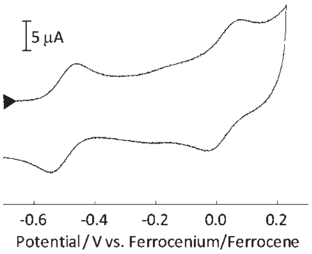

Figure 5. Cyclic voltammogram of **7** (0.5 mM) in 0.1 M *n*-Bu_4NPF_6−CH_2Cl_2 at a sweep rate of 1 V s^{-1}.

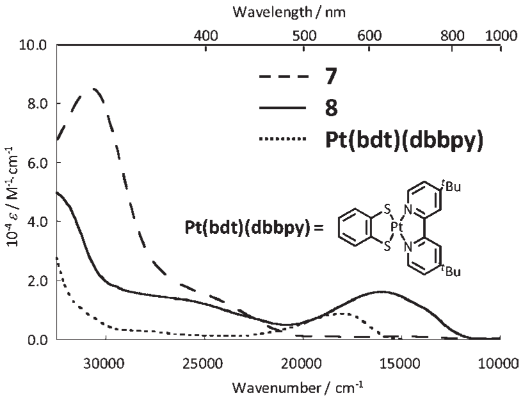

Figure 6. UV−vis−NIR spectra of **7**, **8**, and Pt(bdt)(dbbpy) in dichloromethane.

moieties. Compound **8** displayed a red-shifted and broadened charge-transfer band that reached as far as the NIR region.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, UV−vis spectrum of **6** in dichloromethane (Figure S1), and CIF files for **6**·C_6H_{12} and **7**·$8CH_3CN$. This material is available free of charge via the Internet at http://pubs.acs.org.

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